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Mapping Electron Densities in Porphyrins from High Resolution X-ray Data

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Introduction: Determining electron density distributions from high resolution crystallographic data is a powerful analytical tool for understanding chemical bonding [1]. When applied to porphyrins, such studies can provide insight into the nature of π boding in the porphyrin, bonding between the central metal and axial ligands, distribution of electrons in the metal d-orbitals and porphyrin π-system, oxidation state of the metal, charge on the metal and porphyrin, and the electronic ground state of the metal. Building on the multidisciplinary structural and spectroscopic techniques developed in the Porphyrin Chemistry Program at BNL for addressing the consequences of oxidation in vivo [2], we are now focusing our attention on elucidating the electronic structures of biomimetic porphyrin radicals directly by mapping their electron distributions. Since there are no electron density studies on radicals of any type in the literature, we are using a systematic approach that examines the electron populations in porphyrin radicals and their neutral precursors.

Methods and Materials: Data were collected at 20K with a Bruker CCD detector at wavelengths 0.643Å and 0.394Å. The data were processed and merged with SAINT [3] and the multipole refinements were carried out with XD [4].

Results: The d-orbital populations from two multipole refinements for one of the neutral precursors, Ni(II)octa-ethylporphyrin (NiOEP) [5] are presented in Table 1. An experimental deformation density map for NiOEP is shown in Figure 1.

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References:

[1]. For a general overview of methodology and theory, see P. Coppens., X-ray Charge Densities and Chemical Bonding, Oxford University Press, 1997.

[2]. J. Fajer, *J. Porphyrins Phthalocyanines*, 4, 382(2000) and references therein.

[3]. SAINT Program to Integrate and Reduce Raw Crystallographic Area Detector Data. Bruker Advanced X-ray Solutions. Madison, WI, 1996.

[4]. XD-A Computer Program Package for Multipole Refinement and Analysis of Electron Densities from Diffraction Data. T. Koritsanszky, S. Howard, T. Richter, Z. Su, P. Mallinson, N.K. Hansen, Free University: Berlin, 1995.

[5] E. F. Meyer, Jr., *Acta Cryst*., B28, 2162(1972).

Table 1. Electron Populations in the d-orbitals

	NiOEP (λ=0.394Å)	NiOEP (λ=0.643Å)
data/parameter ratio	32/1	22/1
R-factor	0.027	0.021
Resolution	0.32Å	0.50Å
dx^2-y^2 %	14 [0]*	9
dz^2	21 [25]*	24
dxy	24 [25]*	28
dxz,dyz	41 [50]*	40

*expected for Ni(II) with low spin d^8 configuration

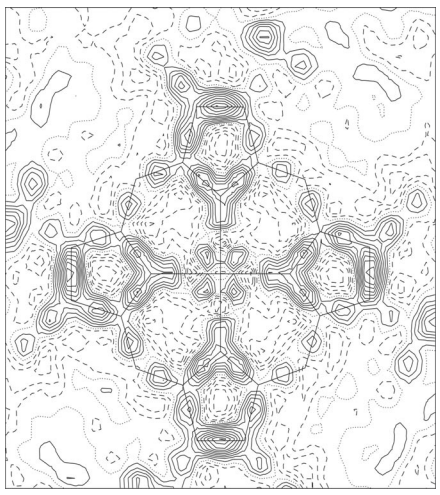

Figure 1. Electron density map in the plane of the nitrogens for NiOEP. Each contour is 0.05 electrons. The zero contour is dotted and negative contours are dashed. Since the molecule is not planar, all the electron density for each atom is not in the above plane and the map appears asymmetrical. The map in the plane of an individual pyrrole ring shows well-defined contours.